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Determining Orientational Structures in Liquid-crystal Phases formed by Bent-core Molecules using Resonant X-ray Diffraction

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Introduction: In recent years, resonant polarized x-ray diffraction (RPXRD) has been used to measure orientational periodicities in chiral smectic phases of liquid-crystal compounds, which are lamellar phases formed by rod-like molecules that may be tilted within the layers [1]. The phases are distinguished only by orientational ordering of the molecules, so ordinary x-ray diffraction does not provide information on this orientational structure. By tuning the incident x-ray energy near the resonant edge of an appropriate atom in the core of the molecules, the scattering is sensitive to the orientation of the molecules. Resonant satellite peaks are observed at $Q_z/Q_0=L+M[(1/\nu+\varepsilon)]$ where $Q_0=2\pi/d$ and d is the layer spacing ($\approx$4nm). L and M are integers and M=0,$\pm$1, or $\pm$2 and ε corresponds to a pitch on the order of microns. This technique can also be applied to liquid-crystal phases formed by "banana-shaped" or bent-core molecules [See Fig. 1]. Surprisingly, some of the phases are chiral, despite the achiral nature of the constituent molecules [2]. As the ordering of the molecules in these phases is largely orientational, RPXRD is an excellent tool for their characterization. One phase is the B2 phase, in which optical experiments suggest that the molecules exhibit a two-layer orientational periodicity [2]. An example of the structure is shown in Fig. 1 where the molecules all tilt in roughly the same direction, but the bend of the molecules (and correspondingly the in-layer polarizations) point in opposite directions in adjacent layers. The other three structures are the remaining permutations of the two possible tilt and bend directions. With the exception of the possible structure with uniform tilt and bend, in any of the other three structures, resonant satellite peaks should occur, corresponding to ν=2. Since there is no long pitch in the B2 phase, ε=0. Calculations demonstrate that the three structures with resonant peaks would yield different intensity ratios of the resonant peaks from two orthogonal polarization states.

Results: In the past year, we have studied both sulfur and chlorine-containing bent-core compounds that exhibit the B2 phase. The presence of resonant-satellite peaks at the half-order position in both compounds confirms the two-layer structure as shown in Fig. 2. One important advance was the observation of the peaks in a geometry in which the sample was placed on surfactant-treated glass to promote alignment. The scattering was from the free-surface. This is a critical achievement since most of the phases do not support free-standing films. Furthermore, to the best of our knowledge we detected the first resonant satellite peaks at the chlorine K-edge in a liquid-crystal compound, thus expanding the number of compounds that can be studied using RPXRD.

Future Directions: We will measure the polarization state of the scattered resonant x-rays and compare intensity ratios to uniquely identify the orientational structure of the B2 phase. We will study other phases formed by bent-core molecules in the free-surface geometry including the B1 phase in which we have observed a resonant peak associated with a possible bi-layer structure of the phase. We will also use RPXRD to continue our studies of a nm-sized incommensurate short helical pitch in the chiral smectic-C_α^* phase.

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References: [1] P. Mach *et al.*, Phys. Rev. E **60**, 6793 (1999). [2] D. R. Link *et al.,* Science **278**, 1924 (1997). [3] A. Cady *et al.*, Liq. Cryst. **29**, 1101 (2002).

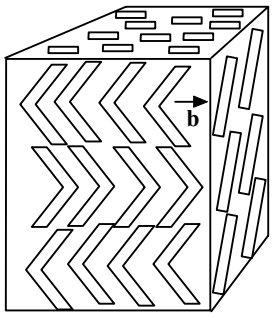

Figure 1. A proposed model for the B2 phase. The molecules are represented by the bows with **b** pointing along the bend [3].

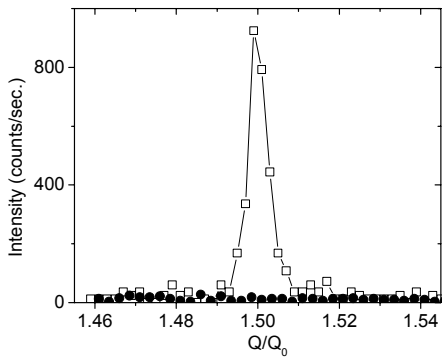

Figure 2. A scan through the resonant satellite peak (open squares) from a free-standing film of the sulfur-containing compound. The black circles are a scan 100eV above the sulfur K-edge [3].